

## XAFS STUDIES OF COAL

G.P. Huffman, F.E. Huggins, N. Shah, F. Lu, and J. Zhao  
CFFLS, 233 Mining & Minerals Res. Bldg., University of Kentucky,  
Lexington, KY 40506-0107

**Keywords:** XAFS, sulfur, trace elements, calcium, chlorine, potassium

### INTRODUCTION

Over the past 10 years, x-ray absorption fine structure (XAFS) spectroscopy has been extensively applied to a variety of problems in coal science. The current paper will review those applications. Because of the fact that XAFS spectroscopy focuses on only one element at a time, it is ideally suited to examining the structure of individual elements in highly heterogeneous materials like coal and its derivatives. We will briefly review XAFS studies of S, Ca, K, Cl, and several trace elements (As, Cr, etc.) in coal. Applications of XAFS in studies of coal combustion, liquefaction, and gasification will be discussed, with emphasis on in situ studies.

### EXPERIMENTAL METHOD

The experimental procedure for obtaining high quality XAFS spectra from various elements in coal is discussed in detail in the references. Briefly, the x-ray beam emitted tangentially from a synchrotron is converted into a high-intensity, monochromatic x-ray beam using a double crystal monochromator. This x-ray beam is then collimated and directed onto the sample to be studied. The monochromator crystals are then turned through a range of Bragg angle in such a manner as to sweep the x-ray energy through the x-ray photoelectric absorption edge (usually the K-edge, occasionally the L-edge) of the element of interest. The x-ray absorption spectrum is measured either by detecting the x-rays that pass through a thin sample without being absorbed, or by detecting the fluorescent x-rays that are emitted by the element of interest after photoelectric absorption of the incident x-rays takes place. Variations on the experiment, such as in situ spectroscopy at elevated temperatures, the use of specialized detectors, etc., are discussed in the references.

The spectra are broken into two regions for detailed computer analysis: the x-ray absorption near edge structure (XANES) region and the extended x-ray absorption fine structure (EXAFS) region. The XANES consists of a series of peaks derived from inner-shell photoelectron transitions to vacant bound levels and scattering resonances. It can be deconvoluted to yield definitive information about the types of electronic bonding present. The EXAFS region can be subjected to a Fourier transform analysis procedure which yields radial distribution functions that are processed to derive information about the local atomic environment; i.e., the type, number, and interatomic distances of neighboring atoms.

### RESULTS

The principal results obtained for a number of different elements of interest in several areas of coal science are briefly summarized below. Topics of current and future interest are also discussed.

#### *Calcium*

One of the earliest coal-related XAFS studies conducted was an investigation of calcium in coal.<sup>(1,2)</sup> It was demonstrated that XAFS spectroscopy detected two major types of calcium: that contained in calcite in bituminous coals, and that bound to oxygen anions in carboxyl groups in lignites and subbituminous coals. The radial distribution functions derived from the XAFS spectra indicated that the carboxyl bound calcium is molecularly dispersed through the macerals.

In situ studies of the carboxyl-bound calcium in lignite were carried out during pyrolysis in He and gasification in CO<sub>2</sub> and He-O<sub>2</sub> at temperatures up to 500 °C.<sup>(3-6)</sup> Only small changes were observed in the calcium spectra, indicating that the calcium undergoes relatively little agglomeration and retains its nearest neighbor oxygen environment with relatively little change under these conditions. Pyrolysis at higher

temperatures (800-1000 °C) causes agglomeration of the calcium to form CaO, which exhibits a distinctive radial distribution function.

During combustion, calcium is rapidly transformed to CaO, which can either react with aluminosilicates to form a Ca-containing aluminosilicate slag, or with SO<sub>2</sub> to form CaSO<sub>4</sub>. XAFS studies combined with other characterization research have demonstrated that these reactions play an important role in slagging and fouling during coal combustion.<sup>(6,7)</sup>

### **Potassium**

Potassium occurs almost exclusively in bituminous coals in the form of illite, which exhibits a very distinctive XANES spectrum.<sup>(8)</sup> Under combustion conditions, the illite melts and contributes significantly to ash deposition problems during combustion.<sup>(7,9)</sup>

In situ XAFS studies of the pyrolysis and gasification reactions of potassium ion-exchanged into lignite have been carried out.<sup>(5)</sup> The ion-exchanged, carboxyl-bound potassium exhibits little change up to 500 °C in He, but converts rapidly to K<sub>2</sub>CO<sub>3</sub> when O<sub>2</sub> is admitted into the hot cell.

### **Chlorine**

The authors have recently completed an XAFS investigation of chlorine in a wide variety of coals.<sup>(10,11)</sup> Chlorine XANES spectra for coals of rank higher than subbituminous are closely similar regardless of chlorine content, rank, and geographic origin, indicating one major mode of occurrence. The evidence indicates that this mode of occurrence is chloride anions in moisture anchored to the surfaces of micropores in coal by organic ionic complexes, such as quaternary amine groups and alkali carboxyl groups. It would appear that the observation of NaCl and other inorganic chlorides is an artifact resulting from precipitation of solid chlorides upon release of moisture from the coal during size reduction and storage.

### **Sulfur**

Extensive XAFS research has been conducted on sulfur in coal in recent years.<sup>(12-18)</sup> It is no exaggeration to say that, as a result of this work, analysis of sulfur XANES spectra has become widely recognized as the best method yet developed for the non-destructive, in situ characterization of the organic sulfur functional forms in coal. Sulfur K-edge XANES can distinguish and quantify with an accuracy of ~±5-10% the amounts of the following major forms of sulfur: thiophene, sulfide, disulfide, elemental sulfur, sulfoxide, sulfone, sulfate, pyrite, and pyrrhotite. S K-edge XANES has been used to study the reactions of sulfur during pyrolysis<sup>(16)</sup> and desulfurization<sup>(17,18)</sup>.

Recently, it has been demonstrated that sulfur L-edge XANES spectroscopy also has great potential for quantification of sulfur functional forms.<sup>(19,20)</sup> The L-edge XANES spectra appear to have better resolution for different sulfur groups than the K-edge spectra. However, the technique is considerably more difficult experimentally, and much model compound calibration work remains to be done. Nevertheless, a preliminary comparison of sulfur K-edge and L-edge results for the analysis of sulfur forms in Mequinzenza lignite gave reasonable results.<sup>(21)</sup>

An excellent review of the XANES methods and other methods of characterizing sulfur in coal has recently been written by Davidson.<sup>(22)</sup>

### **Trace Elements**

Recently, by using an array detector with 13 germanium detection elements, it has been possible to obtain quality XAFS spectra of several critical trace elements in coal.<sup>(23,24)</sup> The primary work to date has been on arsenic and chromium. High quality spectra were obtained at concentration levels as low as 10 ppm. The principal observation of interest for chromium is that there appears to little if any (<5% of the total) Cr<sup>+6</sup> present in either the coals or the combustion ashes investigated to date. Only Cr<sup>+3</sup> is observed. In coal, the form of chromium has been tentatively identified as chromium hydroxide. For arsenic, it is found that most of the arsenic in fresh coals is contained as As in pyrite. In only one coal (Pittsburgh #8, DECS-12) was arsenopyrite observed. Arsenic was also present, however, in all of the coals studied

as arsenate(As(V)). The amount of arsenate was observed to increase fairly rapidly as a result of oxidation under ambient conditions, becoming the dominant form of arsenic present after ~6 months.

### **Current and Future Research**

XAFS spectroscopy has proven to be an excellent method for investigating the structures of the many important elements in coal. Research currently underway or planned for the future that is expected to yield significant results is summarized briefly below.

1. Nitrogen XANES spectroscopy may prove to be as informative as sulfur XANES spectroscopy. Initial studies by Mitra-Kirtley et al.<sup>(25)</sup> look quite promising.

2. XAFS studies of trace elements will undoubtedly increase. Investigation of the reactions of As and Cr during combustion, cleaning or other processes are in progress, and several additional trace elements will be studied.

3. In situ studies under more severe conditions will be emphasized in future research. These include in situ studies of the reactions of such elements as Fe, Ca, K, and S during coal combustion, and studies of liquefaction catalysts at high temperatures and hydrogen pressures.

4. Carbon XANES has recently been shown to have promise in the area of imaging. Using a highly collimated beam, Botto and his co-workers<sup>(26)</sup> have succeeded in imaging macerals in coal by bracketing the characteristic XANES peaks from aromatic and aliphatic carbon and scanning a thin sample.

It appears that this highly versatile technique will continue to have many applications in coal science for years to come.

### **ACKNOWLEDGEMENT**

This work has been supported by the office of Exploratory Research at the Electric Power Research Institute under contract RP-8001, by the U.S. Department of Energy under several contracts, and by the Gas Research Institute.

### **REFERENCES**

1. F. E. Huggins, G. P. Huffman, F. W. Lytle, and R. B. Gregor, Proceedings of the 1983 International Conference on Coal Science, Pittsburgh, PA; pp. 679-682 (International Energy Agency, 1983).
2. G. P. Huffman and F. E. Huggins, ACS Symposium Series No. 264, pp. 159-174, Chemistry of Low-Rank Coals, Ed., H. H. Schobert, Amer. Chem. Soc., 1984.
3. G. P. Huffman, F. E. Huggins, R. G. Jenkins, F. W. Lytle, and R. B. Gregor, Fuel **65**, 1339-1344 (1986).
4. F. E. Huggins, N. Shah, G. P. Huffman, R. G. Jenkins, F. W. Lytle, and R. B. Gregor, Fuel, **67**, 938-941 (1988).
5. F. E. Huggins, N. Shah, G. P. Huffman, R. G. Jenkins, F. W. Lytle, and R. B. Gregor, Fuel, **67**, 1662-7 (1988).
6. G. P. Huffman, F. E. Huggins, A. A. Levasseur, J. Durant, F. W. Lytle, R. B. Gregor, and Arun Mehta, Fuel, **68**, 238-242 (1989).
7. G. P. Huffman, F. E. Huggins, and N. Shah, Progress in Energy and Combustion Science, **16**, #4, 293-302 (1990).
8. G. P. Huffman, F. E. Huggins, R. A. Shoenberger, J. S. Walker, R. B. Gregor, and F. W. Lytle, Fuel **65**, 621-632 (1986).
9. S. Srinivasachar, J. J. Helble, A. A. Boni, G. P. Huffman, F. E. Huggins, and N. Shah, Progress in Energy and Combustion Science, **16**, #4, 243-252 (1990).
10. F. E. Huggins and G. P. Huffman, "An XAFS Investigation of the Form-of-Occurrence of Chlorine in U.S. Coal," Chlorine in Coal, First International Conference, Ed., J. Stringer, Vol.17, Coal Science and Technology, Elsevier, 1991, pp.45-58.
11. F. E. Huggins and G. P. Huffman, "Chlorine in Coal: An XAFS Spectroscopic Investigation," 1993, Fuel, submitted.
12. G.N. George and M.L. Gorbaty, 1989, J. Am. Chem. Soc., **111**, 3182.

13. S.R. Kelemen, M.L. Gorbaty, G.N. George, **1990**, *Fuel*, **69**, 939.
14. G.N. George, M.L. Gorbaty, and S.R. Kelemen, **1991**, *Energy & Fuels*, **5**, 93.
15. G.P. Huffman, S. Mitra, F.E. Huggins, N. Shah, S. Vaidya, and F. Lu, **1991**, *Energy & Fuels*, **5**, 574-581.
16. M. Mehdi Taghiei, F.E. Huggins, N. Shah, and G.P. Huffman, *Energy & Fuels*, **1992**, **6**, 293-300.
17. F.E. Huggins, S.V. Vaidya, N. Shah, and G.P. Huffman, *Fuel Processing Technology*, in press.
18. G. Huffman, N. Shah, F. Huggins, L. Stock, K. Chatterjee, J. Kilbane, M. Chou, and D. Buchanan, "Sulfur Speciation of Desulfurized Coals by XANES Spectroscopy", submitted to *Fuel*; preprint version published in *Amer. Chem. Soc. Div. of Fuel Chem. Preprints*, **1992**, **37(3)**, 1094-1102.
19. M. Kasrai, J.R. Brown, G.M. Bancroft, K.H. Tan, and J.M. Chen, **1990**, *Fuel*, **69**, 411-414.
20. J.R. Brown, M. Kasrai, G.M. Bancroft, K.H. Tan, and J.M. Chen, **1992**, *Fuel*, **71**, 649-653.
21. C.M. White et al., "A Study of Mequinenza Lignite," **1993**, *Fuel*, in press.
22. R.M. Davidson, Organic Sulphur in Coal, **1993**, IEA Coal Research, London.
23. F.E. Huggins, N. Shah, J. Zhao, F. Lu, and G.P. Huffman, *Energy & Fuels*, **7**, 482-489.
24. G.P. Huffman, F.E. Huggins, N. Shah, and J. Zhao, "Speciation of Critical Trace Elements in Coal and Combustion Ash by XAFS Spectroscopy," *International Trace Elements Workshop*, Scottsdale, AR, April, 1993; to be published in *Fuel Processing Technology*.
25. S. Mitra-Kirtley, O.C. Mullins, J. Branthaver, J. Van Elp and S.P. Cramer, **1993**, *Amer. Chem. Soc., Div. Fuel Chem. Preprints*, **38(3)**, 762-768.
26. R.E. Botto, reported during a presentation at the 7th ICCS Conference, Banff, Canada, 1993.